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13. ABSTRACT (Maximum 200 words) This project brought together three distinct experimental methods in an integrated investigation of the phase behavior, structure and properties of block copolymers in the vicinity of the order-disorder transition. Anionic polymerization of polydiene diblock copolymers followed by catalytic hydrogenation was used to produce three classes of model saturated hydrocarbon materials. Dynamic mechanical spectroscopy and large amplitude dynamic shearing were employed to probe and manipulate, respectively, the melt state microstructure. Small angle neutron scattering (SANS) experiments provided detailed information regarding the structure of the materials. A significant achievement during this work was the development of a dynamic shearing device that could be operated <i>in situ</i> with a SANS instrument. Together with the spectrum of materials produced, this combined scattering-rheology technique has led to a qualitative improvement in our understanding of block copolymer phase behavior, and uncovered a rich polymorphism that is accompanied by dramatic variations in physical properties. Two new parameters have been shown to play a crucial role in determining block copolymer phase behavior. The degree of polymerization, controls the extent of composition fluctuations which strongly affects the types of phases encountered near the order-disorder transition. Conformational asymmetry, which is controlled by the block volume and radius of gyration, leads to different phases on either side of the phase diagram. These effects have not been accounted for theoretically.					
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COMPLETED PROJECT SUMMARY

TITLE: Phase behavior, structure, and properties of model block copolymers

PRINCIPAL INVESTIGATOR: Frank S. Bates

INCLUSIVE DATES: 15 Apr 90 - 14 Oct 93

CONTRACT/GRANT NUMBER: 61103D 3484/RS

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- PUBLICATIONS:
- 1.) "Epitaxial Growth and Shearing of the Body Centered Cubic Phase in Diblock Copolymer Melts," K. A. Koppi, M. Tirrell, F. S. Bates, K. Almdal and K. Mortensen, submitted to J. Rheology
 - 2.) "Complex Phase Behavior of PS-PI Diblock Copolymers near the Order-Disorder Transition," S. Förster, A. K. Khandpur and F. S. Bates, submitted to Macromolecules
 - 3.) "Complex Layered Phases in Asymmetric Diblock Copolymers," I. W. Hamley, M. D. Gehlsen, A. K. Khandpur, K. A. Koppi, J. H. Rosedale, M. F. Schulz, F. S. Bates, K. Almdal and K. Mortensen, in preparation, to be submitted to J. Phys. II France
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- 11.) "Order, Disorder, and Fluctuation Effects in an asymmetric Poly(ethylene-propylene)-poly(ethylene) Diblock Copolymer," K. Almdal, F. S. Bates and Kell Mortensen, *J. Chem. Phys.*, 96, 9122 (1992)
- 12.) "Critical Dynamics of Polymer Blends," P. Stepanek, T. P. Lodge, C. Kedrowski and F. S. Bates, *J. of Chem. Phys.*, 94, 8289 (1991)
- 13.) "Polymer-Polymer Phase Behavior," F. S. Bates, *Science*, 251, 898 (1991)

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This program was initiated with two primary objectives. Firstly, to develop and characterize a new class of model block copolymers, and secondly, to study the thermodynamic and dynamic behavior of these materials in the vicinity of the order-disorder transition. The project brought together three distinct experimental methods in an research program that addressed the phase behavior, structure and properties of block copolymers. Anionic polymerization of polydiene diblock copolymers followed by catalytic hydrogenation was used to produce three classes of model saturated hydrocarbon materials. Dynamic mechanical spectroscopy and large amplitude dynamic shearing were employed to probe and manipulate, respectively, the melt state microstructure. Small angle neutron scattering (SANS) experiments provided detailed information regarding the structure of the materials. A significant achievement during this work was the development of a dynamic shearing device that could be operated *in situ* with a SANS instrument. Together with the spectrum of materials produced, this combined scattering-rheology technique has led to a qualitative improvement in our understanding of block copolymer phase behavior, and uncovered a rich polymorphism that is accompanied by dramatic variations in physical properties. Two new parameters have been shown to play a crucial role in determining block copolymer phase behavior. The degree of polymerization, controls the extent of composition fluctuations which strongly affects the types of phases encountered near the order-disorder transition. Conformational asymmetry, which is controlled by the block volume and radius of gyration, leads to different phases on either side of the phase diagram. These effects have not been accounted for theoretically. Thus, both research objectives have been met, while concurrently expanding the spectrum of microstructures, and associated physical properties, available for applications with this important class of materials.

Phase Behavior, Structure, and Properties of Model Block Copolymers

AFOSR - 90-0207 15 Apr. 90 - 14 Oct. 93

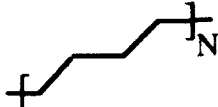
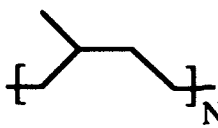

Final Technical Report

Principal Investigator - Frank S. Bates

This project brought together three distinct experimental methods in an integrated investigation of the phase behavior, structure and properties of block copolymers in the vicinity of the order-disorder transition. Anionic polymerization of polydiene diblock copolymers followed by catalytic hydrogenation was used to produce three classes of model saturated hydrocarbon materials. Dynamic mechanical spectroscopy and large amplitude dynamic shearing were employed to probe and manipulate, respectively, the melt state microstructure. Small angle neutron scattering (SANS) experiments provided detailed information regarding the structure of the materials. A significant achievement during this work was the development of a dynamic shearing device that could be operated *in situ* with a SANS instrument. Together with the spectrum of materials produced, this combined scattering-rheology technique has led to a qualitative improvement in our understanding of block copolymer phase behavior, and uncovered a rich polymorphism that is accompanied by dramatic variations in physical properties. The remainder of this report is organized as follows. A summary of progress during each of the three years of the project is presented, followed by recommendations for future work. The personnel that have contributed to this effort and the resulting publications are then listed.

Year 1 - During the first year of this project two classes of saturated hydrocarbon block copolymers were developed. Poly(ethylene-propylene)-poly(ethylethylene) (PEP-PEE) diblock copolymers were prepared by a two-step process. Nearly monodisperse *cis* 1,4 polyisoprene-1,2 polybutadiene diblock copolymers were anionically polymerized using previously reported methods (1). This unsaturated polymer was then completely hydrogenated (or deuterated) using a

Table 1
Model Polyolefins

Polymers	Segment Structure	$\rho(23^\circ\text{C})$ (g/cm ³)	$b(25^\circ\text{C})$ (Å)	$10^7\beta$ (cm ⁻¹)
PE [poly(ethylene)]		^a 0.855	^a 8.8	1.19
PEP [poly(ethylene-propylene)]		0.855	8.0	0.78
PEE [poly(ethylene)]		0.869	5.0	0.39

^a Extrapolated from above the melt temperature.

calcium carbonate supported palladium catalyst. Poly(ethylene)-poly(ethylene-propylene) (PE-PEP) diblock were similarly obtained from 1,4 polybutadiene-*cis* 1,4 polyisoprene diblocks. (Structural sketches of all three diblock copolymers developed during the course of this work are provided in Table 1.) Eleven PEP-PEE and three PE-PEP polymers were prepared. These materials were used to establish the molecular weights required to locate each type of polymer near the order-disorder transition (ODT).

Phase behavior was probed using a Rheometrics RSA II solids analyzer, which was acquired with support from this grant. A combination of isochronal temperature scans, and isothermal frequency scans was employed, in order to quantitatively determine the ODT temperature. At temperatures above T_{ODT} block copolymer melts behave like Newtonian liquids while below T_{ODT} they exhibit properties intermediate to solids and liquids. A major breakthrough was the discovery of four distinct ordered phases in a PEP-PEE specimen containing 65% PEP, i.e., $f_{PEP} = 0.65$ (2). This was the first demonstration of multiple ordered phase behavior in a block copolymer melt.

SANS measurements, conducted at Oak Ridge National Laboratory, and Risø National Laboratory (Denmark) on deuterium labeled specimens, provided independent confirmation of the rheological results. The technique of shear orientation was demonstrated using a prototype shearing device operated at the Minnesota laboratory. This method also led to a preliminary assessment of the multiple ordered phase symmetries in the $f_{PEP} = 0.65$ specimen (3). SANS measurements on compositionally symmetric samples ($f_{PEP} \approx 0.5$) demonstrated that composition fluctuation effects play a key role in the vicinity of the order disorder, leading to polymer coil stretching that is not anticipated by mean-field theory.

Overall, progress in Year 1 provided substantial evidence that state-of-the art theory and experiment had not anticipated the complex nature of block copolymer phase behavior and properties near the order-disorder transition.

Year 2 - The materials base was expanded significantly in the second year of the project.

Several additional PEP-PEE (for a total of 15), and five new PE-PEP (for a total of 8) specimens

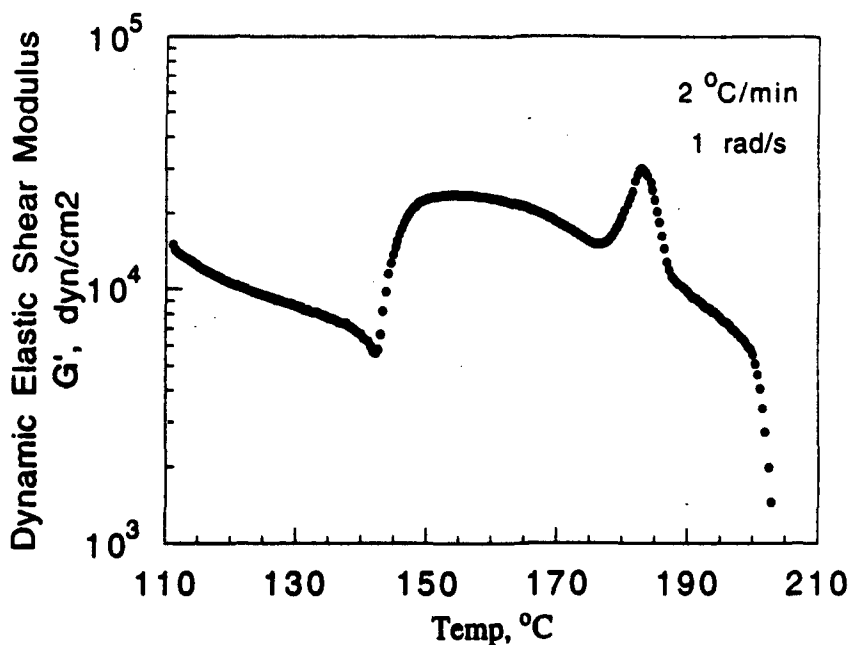


Figure 1. Dynamic elastic modulus for $f = 0.65$ PE-PEE measured at a constant heating rate of $2^{\circ}\text{C}/\text{min}$ and at a constant frequency of 1 rad/s . This specimen exhibits four ordered phases that are associated with the transitions in G' .

with various compositions were prepared. A third system, poly(ethylene)-poly(ethylethylene) (PE-PEE) was also developed by hydrogenating 1,4 polybutadiene - 1,2 polybutadiene precursor molecules. Six PE-PEE materials, including several that were deuterium labeled were synthesized near the ODT.

Dynamic mechanical spectroscopy revealed that the initial evidence for multiple ordered phase behavior in the $f_{PEP} = 0.65$ specimen was not anomalous. A $f_{PE} = 0.65$ PE-PEE sample was found to exhibit a similar response, as illustrated in Figure 1. Several distinct ordered phases were also revealed in $f_{PE} = 0.65$ and 0.40 PE-PEP specimens. SANS measurements conducted at Risø and the National Institute of Standards and Technology (NIST) suggested that the multiple phases represented intermediate states between lamellae and hexagonally packed cylinders.

A significant conclusion that emerged from the work with three different block copolymers was the notion of an asymmetric phase diagram. Classical theoretical treatments of block copolymer phase behavior produce three types of ordered phases (bcc spheres, hexagonally packed cylinders, and lamellae) that are symmetrically distributed around $f = 0.5$. The research with PEP-PEE, PE-PEE, and PE-PEP had revealed a qualitatively different set of results. At $f = 0.65$ four (PEP-PEE and PE-PEE) or three (PE-PEP) ordered phases had been found, while for $f = 0.35$ only one ordered phase occurred. This asymmetry suggested that another molecular factor, conformational asymmetry, was important in block copolymer phase behavior.

PE, PEE, and PEP are characterized by different statistical segment lengths b ,

$$b = \frac{R_g}{(N/6)^{1/2}} \quad (1)$$

where R_g is the unperturbed (homopolymer) radius of gyration and N is the degree of polymerization. These differences in coil conformation lead to variations in the space-filling criteria in an ordered block copolymer, and necessitate corrections to classical statistical mechanical descriptions that assume a single common value of b . A convenient parameter that combines the space and volume filling characteristics into a single term is given by,

$$\beta^2 = \frac{R_g^2}{V} = \frac{b^2 N / 6}{v_o N} = \frac{b^2}{v_o 6} \quad (2)$$

where v_o is the statistical segment volume. For a diblock copolymer, or a binary blend, conformational symmetry can be expressed by,

$$\epsilon = \frac{\beta_1^2}{\beta_2^2} \quad (3)$$

where $\epsilon = 1$ indicates a symmetric, and $\epsilon \neq 1$ an asymmetric system. The asymmetric block copolymer phase behavior correlates with $\epsilon \neq 1$.

The values of N required to induce ordering in the polyolefin diblock copolymers was also found to correlate with ϵ . For PE-PEE, PEP-PEE and PE-PEP, $\epsilon = 3.1, 2.1$ and 1.5 while $N_{ODT} \approx 500, 1000$ and 2000 , respectively. This suggests that the classical theoretical description of the Flory-Huggins segment-segment interaction parameter should be expanded to include non-ideal entropic contributions due to conformational asymmetry, a new concept that was reported in a publication (4). Subsequent work on block copolymer phase behavior has been guided by this concept.

Year 3 - In the final year of the program the synthetic effort was accelerated, bringing the total number of polyolefin specimens produced to fifty four: 14 PE-PEP, 17 PE-PEE and 23 PEP-PEE. Rheological and SANS experimentation led to the construction of two types of phase diagrams that are illustrated in Figures 2 and 3. In Figure 2, the findings for the PEP-PEE and PE-PEE polymers are reported. These systems produced essentially identical results. Confirmed order-order phase transitions are indicated by solid curves, while unconfirmed phase boundaries are denoted by dashed curves. A prominent feature is the asymmetry in phase types above and below $f = 1/2$. For $f > 1/2$ there is clear evidence for two new intermediate layered phases,

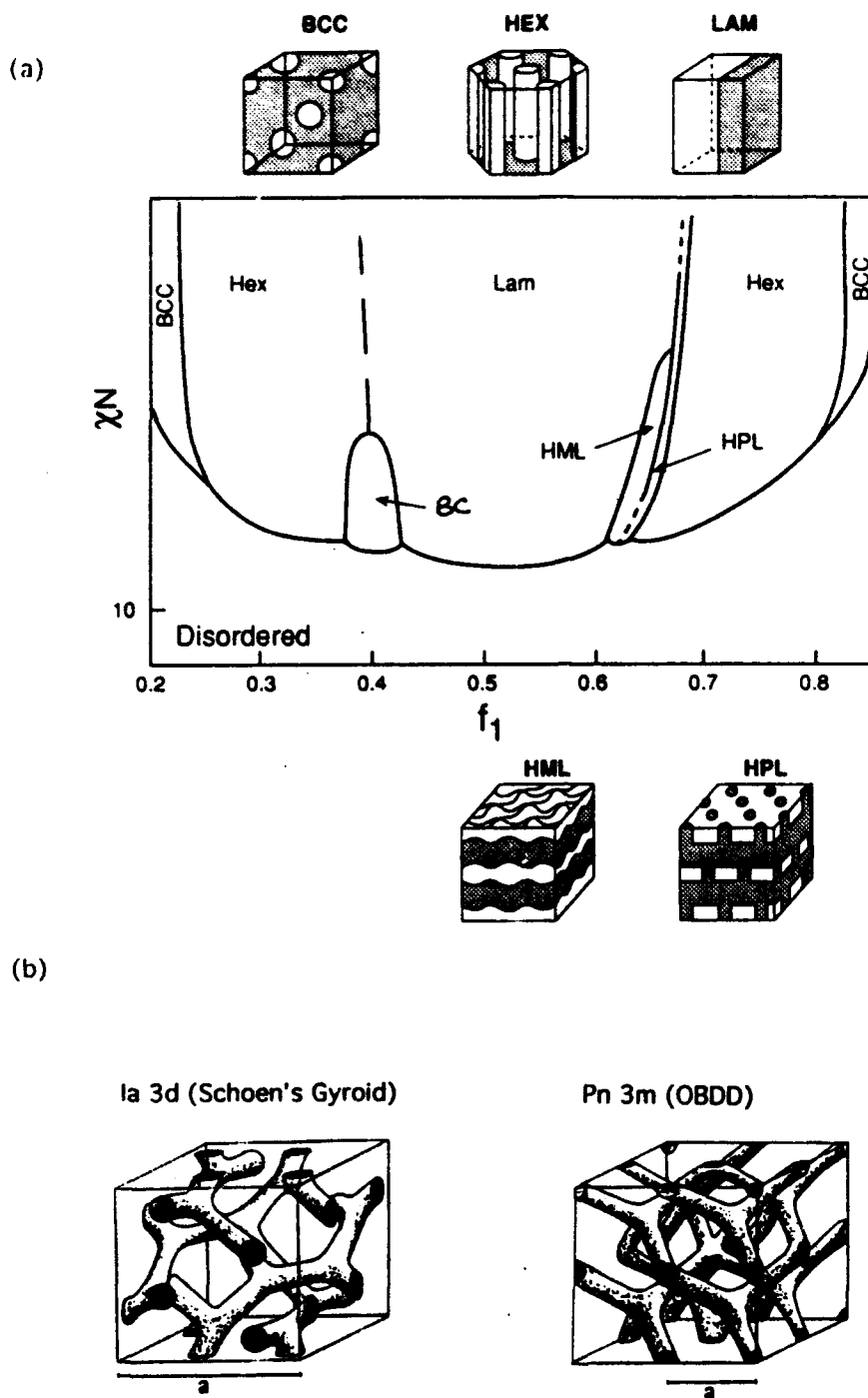


Figure 2. (a) Phase diagram for PEP-PEE and PE-PEE diblock copolymer melts. The phase assignments have been made based on SANS and rheology measurements from over forty specimens. Several of the features shown here have been reported recently (2,3) although the complete phase diagram has not been published. The pronounced differences for $f < 1/2$ and $f > 1/2$ can be traced to conformational asymmetry. BC refers to bicontinuous phases, and includes OBDD and Ia3d as shown in (b).

hexagonally modulated lamellae (HML) and hexagonally perforated lamellae (HPL). Between $f = 0.39$ and $f = 0.44$ complex ordered bicontinuous phases were discovered. One new cubic phase, referred to as Schoen's Gyroid (Ia3d space group) was confirmed and a second, the ordered bicontinuous double diamond (OBDD) phase may also occur. A remarkable feature is the localization of the bicontinuous phases to a region of phase space near the ODT. Previous reports of the OBDD phase in polystyrene-polyisoprene block copolymers have concluded that an OBDD channel exists at all values of χN between lamellae and cylinders. This work has led to the important conclusion that for $T \ll T_{ODT}$ the cubic phases most likely exist in a metastable state, much like one finds in metastable inorganic materials such as martensite.

Figure 2 reveals a somewhat different phase behavior for the PE-PEP polymers. Here the HML and HPL phases are found on both sides of the phase diagram, and there is no bicontinuous window. A major conclusion that emerges from this project is that **both** conformational symmetry

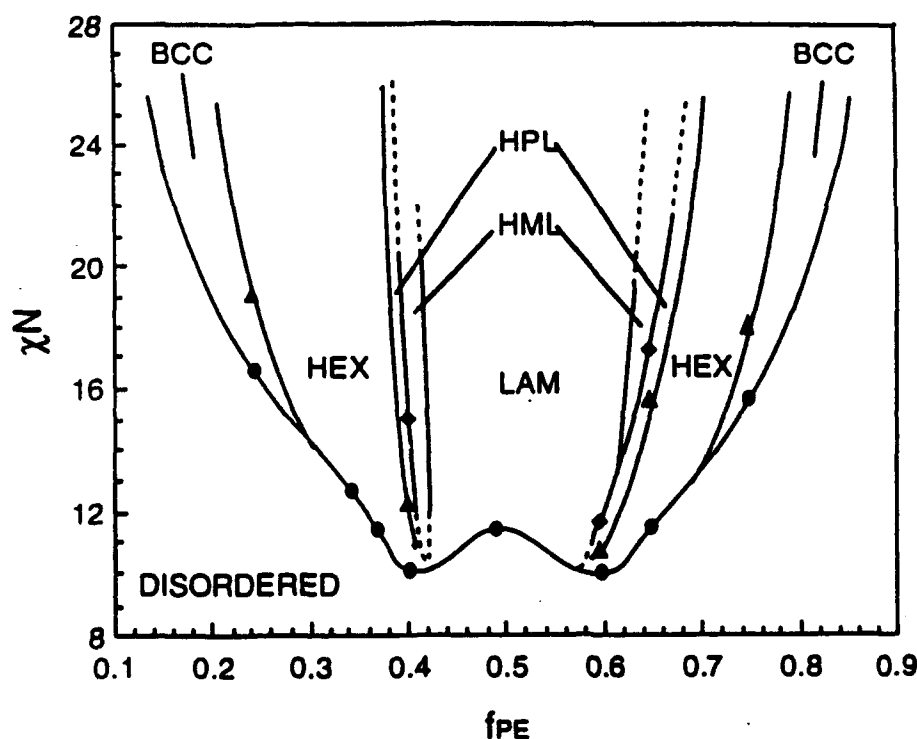


Figure 3. Experimental phase diagram for PE-PEP diblock copolymers. The solid points indicate documented order-order, and order-disorder transitions. The associated microstructures are identified in Figure 2. Bicontinuous phases have not been found in this relatively symmetric system.

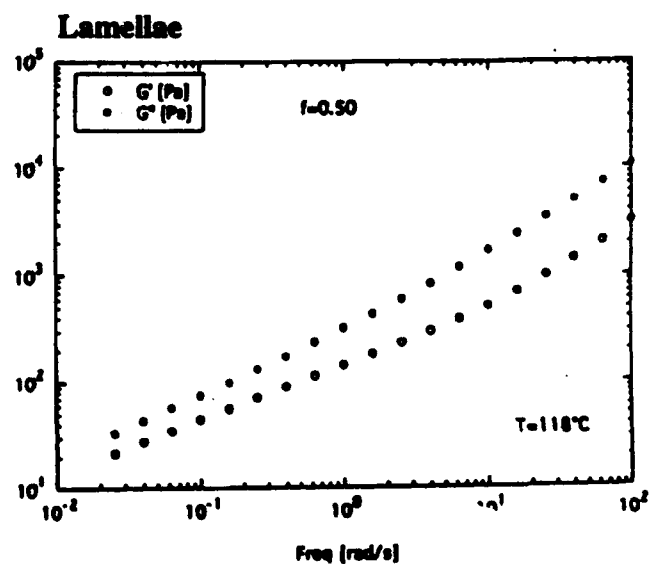
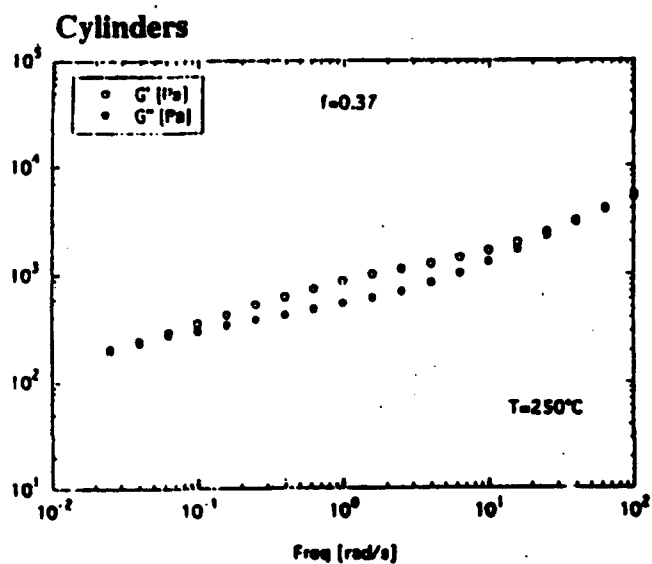
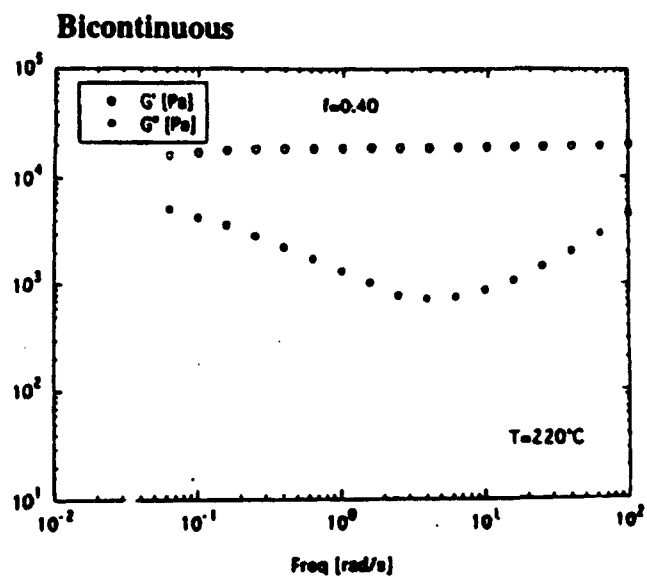
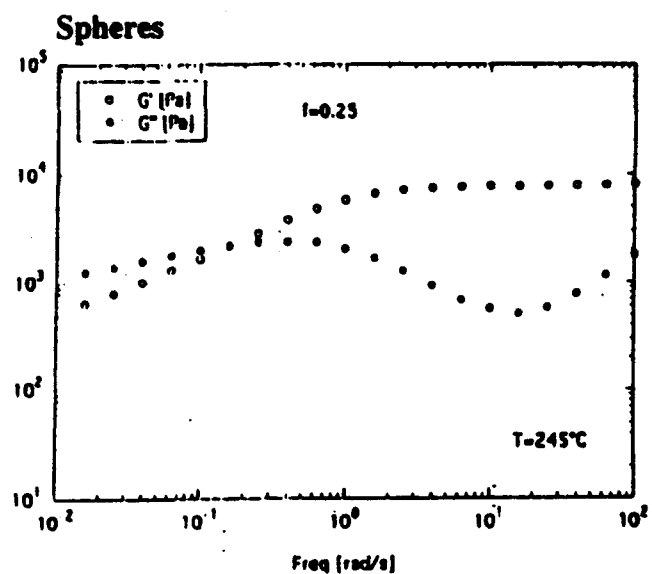


Figure 4. Illustrations of the rheological characteristics of various types of microstructures found in ordered PE-PEE block copolymers.

and N influence block copolymer phase complexity. Increasing N has been shown to decrease the effects of composition fluctuations near the ODT. The loss of the bicontinuous phases in PE-PEP indicates that fluctuation effects play an important role in ordered, as well as disordered block copolymers.

Establishing the symmetry of the HML, HPL and bicontinuous cubic phases required the development of a new experimental technique. In the final year of this project a specially designed shearing device that could be operated in conjunction with SANS measurements was constructed and placed in operation. (This project was conducted in collaboration with the Center for Interfacial Engineering (CIE) at the University of Minnesota, a NSF engineering research center). With this device, specimens could be sheared at specific temperatures over a wide range of shear rates. Subsequent heating or cooling through order-order phase transitions while conducting SANS measurements provides unique access to field induced changes in the ordered symmetry. With this tool, the symmetry of the ordered phases previously identified rheologically could be established. Figures 2 and 3 have resulted from such experimentation. This new technique represents a major advance in the field of polymer science and engineering.

Knowledge of the f , χ , N and ϵ dependence of the phase behavior of polyolefin block copolymers has provided the basis for exploring and establishing structure-property relationships in these complex materials. In Figure 4 representative isothermal dynamic mechanical frequency scans of four PE-PEE materials, characterized by different ordered microstructures, are presented. Although a detailed discussion of these plots is beyond the scope of this report, it is quite obvious that each phase has a distinctive mechanical response. Furthermore, each also exhibits a different, and rate dependent, response to deformation. This research has provided a new foundation for the development and commercial exploitation of this fascinating class of materials.

Recommendation for Future Work

The results of this research program suggest that a variety of interesting and mechanically unique structures can be prepared from block copolymer melts. All this work was accomplished using nearly monodisperse diblock copolymers. Commercial applications would require a robust

means of controlling f and N that did not rely on precise chemical synthesis. Therefore, a logical next step is to investigate mixtures of block copolymers. By mixing two or more components the properties of a material could be easily controlled, as is commonly practiced at large industrial scales. However, the delicate balance of molecular factors that lead to the formation of the modified layered and bicontinuous phases could be disrupted by blending, or could lead to additional, and perhaps more useful phases. Clearly, blending offers many new possibilities, and should be investigated in future work.

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1. F.S. Bates, J.H. Rosedale, H.E. Bair and T.P. Russell, *Macromolecules* **22**, 2557 (1989).
2. K. Almdal, K.A. Koppi, F.S. Bates and K. Mortensen, *Macromolecules* **25**, 1743 (1992).
3. I.W. Hamley, I.A. Koppi, J.H. Rosedale, F.S. Bates, K. Almdal and K. Mortensen, *Macromolecules* **26**, 5959 (1993).
4. F.S. Bates, M.F. Schulz, J.H. Rosedale and K. Almdal, *Macromolecules* **25**, 5547 (1992).

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Kurt Koppi - Ph.D., November 1993. Now at Dow

Publications derived in full or part from AFOSR 90-0207:

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